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(54) **Green, Turquoise and Blue Pigments Containing Phosphate**

(57) The present invention relates to new inorganic green to blue phosphate pigments of formula $M(I)M(II)PO_4$. M(I) stands for the alkali metals potassium, sodium and lithium, and M(II) for the bivalent metals zinc, copper and cobalt. For a sum of the bivalent metals of 1.00, the respective single concentration ranges from 0.00 to 0.99. The methods of preparation of the pigments and their use are also subjects of this application.

Description

Of the inorganic compounds containing phosphate, white $Zn_3(PO)_2.xH_2O$ (x = 2-4) and green $CrPO_4 \cdot 3H_2O$ find practical application as corrosion protection pigments. For the color range green, turquoise, blue, the following described phosphate-free inorganic compounds have become of interest in the art:

chrome oxide green	α-Cr_2O_2, hexagonal exkolaite lattice
turquoise to green	(Zn,Co)O, hexagonal wurtzite mixed phases
cobalt blue	$(Co,Zn)(Al,Cr)_2O_4$, cubic mixed phases, spinels and/or their further cubic mixed phases with γ-Al_2O_3
ultramarine blue	$Na_8[Al_6Si_6O_{24}]S_{2-4}$, cubic sodalith lattice
Berlin blue	$KFe[Fe(CN)_6]$, cubic lattice
manganese blue	$Ba(S, Mn)O_4$, rhombic barite lattice
zirconium blue	$Zr(Si, V)O_4$, tetragonal zirconium lattice

Some of the said green, turquoise and blue pigments have no special purity of color, high proportions of costly metal oxides (Co, Zr), low chemical and thermal stability, and they are not always physiologically unobjectionable.

Also, some of the pigments can be prepared only at very high temperatures, under special artificial gaseous atmospheres or in complicated calcining processes that take weeks, subject to strict ecological precautions. Besides, the

complete palette from green through turquoise to blue cannot be realized in a single system.

The object of the invention is to prepare temperature-stable green, turquoise and blue pigments in a single system, hue and intensity being generated by varying the quantity of chromatic copper and/or cobalt ions with the quantity of achromatic zinc ions in the alkali phosphate system (K, Na, Li). The object of the invention may also consist, while preserving hue and intensity, in replacing a portion of the costly cobalt with considerably cheaper copper. The new inorganic green, turquoise and blue pigments are systems of the composition $M(I)M(II)PO_4$, where M(I) = K and/or Na and/or Li and M(II) = x Zn and/or y Cu and/or z Co, subject to the following additional condition:

$$0.00 \leq x \leq 0.99;\ 0.00 \leq y \leq 0.99;\ 0.00 \leq z \leq 0.99, \text{ and } x + y + z = 1$$

The new pigments are prepared by calcining mixtures of the quantities specified in the equations for oxides and/or phosphates of K, Na, Li; Zn, Cu, Co, or compounds yielding these upon calcining in air (e.g. alkali metal or ammonium carbonates, nitrates, phosphates, acetates, formates, hydroxides) in a certain temperature range under an atmosphere containing oxygen, preferably air, cooling the product, and comminuting to pigment fineness.

To control pigment particle size in the interest of desired properties, a precipitation method of preparing the pigments or their starting compounds may be advantageous. By choice of concentration of the cationic and anionic

components, mode of precipitation, temperature of precipitation and drying, for example in the $KM(II)PO_4$ system, mixed phases containing or free from water of crystallization can be prepared, and converted into the desired new pigments by drying or calcining alone.

Depending on content of water-soluble salts, the product of calcining or precipitation may be washed with water, filtered off, dried and ground. Calcining temperature and exposure time, as well as the presence of small amounts of mineralizers promoting crystallization, are of decisive significance for the properties of the new green, turquoise and blue pigments. The calcining or drying temperature is between 80° and 1100°C, preferably between 300° and 900°C. The calcining time ranges as a rule between 0.1 and 10 hours, preferably between 0.5 and 5 hours.

The pigments thus prepared have specific BET surface areas (G. Brunauer, P.H. Emmet and H. Teller, *J.Am.Chem.Soc. 60 309* (1938), between 0.01 and 300, preferably between 0.1 and 100 m^2/g.

Tables 1-3 list examples of the preparation of 5 g each of pigment of the specified composition. Corresponding amounts of analytically pure starting substances are carefully mixed in an agate dish. The mixture is calcined in a platinum crucible following the specified calcining program at each temperature for 1 hour in air, carefully ground after cooling and again calcined in air for the same length of time at the next higher temperature. The visually rated color of the products highest calcined and ground to pigment fineness is given in the last column of the tables.

Table 1 gives the data for the $M(I)M(II)PO_4$ pigments containing at least potassium, Table 2 for those containing at least sodium, and Table 3 for those containing at least lithium. It will be seen that according to the qualitative visual assessment all colors occur from luminous green, sea green, luminous turquoise, blue-turquoise, light blue, gentian blue, luminous blue, luminous ultramarine blue to violet blue. By changing the quantity of the non-chromatic zinc ion in the new green, turquoise and blue phosphate pigments, intensity and saturation can be varied so that with decreasing zinc content, spectral density and color intensity increase. For given composition of the bivalent cations (Zn, Cu, Co), to a lesser extent the color can be influenced by the proportions of M(I) cations (K, Na, Li). Very generally, the quality of the pigments improves in transition from Li through Na to K, the discontinuity in properties being greatest at the change from Li to Na.

Table 4 shows the relative color intensities determined according to German Standard DIN 53,234 for $K(Co, Cu, Zn)PO_4$ pigments of various compositions. The color intensity of specimen No. 4.1, composition $KCo_{0.10}Zn_{0.90}PO_4$, is equated to 100 for comparison.

We see that for constant cobalt content of 0.10, the color intensity rises upon replacement of achromatic zinc with chromatic copper cation from 100 through 220 and 240 to 260, if the copper content in the formula rises from 0 through 0.20 and 0.45 to 0.60. A color intensity similar to that of $KCo_{0.10}Cu_{0.60}Zn_{0.30}PO_4$ (No. 4.4) is exhibited by the copper-free compound $KCo_{0.25}Zn_{0.75}PO_4$ (No. 4.6).

At constant cobalt content of 0.25 (No. 4.6), the color intensity rises upon replacement of the achromatic zinc by the chromatic copper ion from 262 through 367 to 404, if the copper conent in the formula rises from 0 through 0.38 to 0.50 (Nos. 4.7; 4.8).

The new green, turquoise and blue phosphate pigments according to the invention represent novel inorganic pigments. At an accustomed cobalt to copper metal price ratio of about 6:1, an economic advantage is gained in certain color series, since the color intensity of the pigments can be substantially enhanced merely by increasing the Cu content. (Compare examples 4.1-4.4 and 4.6-4.8.)

The visual color impression of the blue pigments hardly varies for constant cobalt content if the colorless zinc is replaced by the chromatic copper.

The esthetically most satisfactory greenish blue shade of the manganese blue and luminous gentian blue results from certain preparations in the new class of pigments that represent an enrichment of the inorganic pigments located in this color range. The new pigments may be employed to color building materials, varnishes and dispersion paints, plastics, fibers and papers as well as ceramics.

The invention will be illustrated by some examples in the following Tables 1-4.

Table 1

M(I)M(II)PO_4 pigments containing potassium

No.	System	Calcining Program [° C]	Color
1.1	$KZn_{0,99}Cu_{0,01}PO_4$	300/500/700	pale turquoise white
1.2	$KZn_{0,75}Cu_{0,25}PO_4$	500/700/800	luminous turquoise
1.3	$KZn_{0,50}Cu_{0,50}PO_4$	300/500/800	luminous blue
1.4	$KZn_{0,33}Cu_{0,67}PO_4$	500/700/800	light (manganese) blue
1.5	$KZn_{0,25}Cu_{0,75}PO_4$	300/500/800	luminous green
1.6	$KZn_{0,01}Cu_{0,99}PO_4$	500/700/800	luminous turquoise
1.7	$KZn_{0,99}Co_{0,01}PO_4$	300/500/700	pale bluish white
1.8	$KZn_{0,75}Co_{0,25}PO_4$	300/500/700	full luminous blue
1.9	$KZn_{0,50}Co_{0,50}PO_4$ (solid)	500/700/800	full luminous blue
1.10	$KZn_{0,50}Co_{0,50}PO_4$ (precipitate)	100/750	full luminous blue
1.11	$KZn_{0,25}Co_{0,75}PO_4$	500/700/800	full luminous deep blue
1.12	$KZn_{0,01}Co_{0,99}PO_4$	500/700/800	full luminous deep blue
1.13	$KCo_{0,75}Cu_{0,25}PO_4$	500/700/800	luminous ultramarine blue
1.14	$KCo_{0,50}Cu_{0,50}PO_4$	500/700/800	luminous ultramarine blue
1.15	$KCo_{0,33}Cu_{0,67}PO_4$	500/700/800	luminous pure blue
1.16	$KCo_{0,50}Cu_{0,25}Zn_{0,25}PO_4$	300/500/700	full luminous blue
1.17	$KCo_{0,25}Cu_{0,50}Zn_{0,25}PO_4$	500/700/800	luminous blue
1.18	$KCo_{0,25}Cu_{0,25}Zn_{0,50}PO_4$	300/500/650	luminous blue
1.19	$K_{0,50}Na_{0,50}Cu_{0,33}Co_{0,33}Zn_{0,34}PO_4$	300/500/700	luminous ultramarine blue
1.20	$K_{0,90}Na_{0,10}Cu_{0,33}Co_{0,33}Zn_{0,34}PO_4$	300/500/650	luminous blue
1.21	$K_{0,33}Na_{0,34}Li_{0,33}Cu_{0,33}Co_{0,33}Zn_{0,34}PO_4$		

Table 2

$M(I)M(II)PO_4$ pigments containing sodium

No.	System	Calcining Program [° C]	Color
2.1	$NaZn_{0,99}Cu_{0,01}PO_4$	300/500/700	turquoise-white
2.2	$NaZn_{0,75}Cu_{0,25}PO_4$	300/500/650	luminous turquoise
2.3	$NaZn_{0,50}Cu_{0,50}PO_4$	300/500/700	bluish turquoise
2.4	$NaZn_{0,25}Cu_{0,75}PO_4$	300/600/650	turquoise blue
2.5	$NaZn_{0,01}Cu_{0,99}PO_4$	500/600/650	turquoise
2.6	$NaZn_{0,90}Co_{0,10}PO_4$	300/500/650	luminous blue
2.7	$NaZn_{0,75}Co_{0,25}PO_4$	300/500/650	luminous deep blue
2.8	$NaZn_{0,50}Co_{0,50}PO_4$	300/500/650	luminous deep blue
2.9	$NaZn_{0,25}Co_{0,75}PO_4$	300/500/650	luminous blue
2.10	$NaZn_{0,01}Co_{0,99}PO_4$	500/700/800	luminous blue
2.11	$NaCo_{0,50}Cu_{0,50}PO_4$	300/500/650	greenish blue gray
2.12	$NaCo_{0,25}Cu_{0,75}PO_4$	300/500/650	sea green
2.13	$NaCo_{0,10}Cu_{0,90}PO_4$	500/650/700	gray turquoise
2.14	$NaCo_{0,50}Cu_{0,25}Zn_{0,25}PO_4$	300/500/650	luminous cobalt blue
2.15	$NaCo_{0,25}Cu_{0,50}Zn_{0,25}PO_4$	300/500/650	full steel blue
2.16	$NaCo_{0,25}Cu_{0,25}Zn_{0,50}PO_4$	300/500/650	luminous cobalt blue
2.17	$NaCo_{0,33}Cu_{0,33}Zn_{0,34}PO_4$	300/500/650	luminous cobalt blue
2.18	$Na_{0,50}Li_{0,50}Co_{0,10}Cu_{0,45}Zn_{0,45}PO_4$	300/500/650	gentian blue
2.19	$Na_{0,10}Li_{0,90}Co_{0,10}Cu_{0,45}Zn_{0,45}PO_4$	300/500/650	gentian blue

Table 3

M(I)M(II)PO_4 pigments containing lithium.

No.	System	Calcining Program [° C]	Color
3.1	$LiZn_{0,99}Cu_{0,01}PO_4$	300/500/700	turquoise-blue
3.2	$LiZn_{0,75}Cu_{0,25}PO_4$	300/500/700	light greenish turquoise
3.3	$LiZn_{0,50}Cu_{0,50}PO_4$	300/500/700	luminous blue turquoise
3.4	$LiZn_{0,25}Cu_{0,75}PO_4$	300/500/750	luminous blue turquoise
3.5	$LiZn_{0,01}Cu_{0,99}PO_4$	300/500/750	luminous blue turquoise
3.6	$LiZn_{0,75}Co_{0,25}PO_4$	300/500/750	cobalt blue
3.7	$LiZn_{0,50}Co_{0,50}PO_4$	300/500/750	bluish mauve
3.8	$LiZn_{0,01}Co_{0,99}PO_4$	300/500/750	mauve
3.9	$LiCo_{0,50}Cu_{0,50}PO_4$	300/500/750	mauve
3.10	$LiCo_{0,25}Cu_{0,75}PO_4$	300/500/750	steel blue
3.11	$LiZn_{0,70}Co_{0,10}Cu_{0,20}PO_4$	300/500/750	full luminous mauve
3.12	$LiZn_{0,34}Co_{0,33}Cu_{0,33}PO_4$	300/500/750	full mauve

Table 4

Color intensity (DIN 53.234) of K(Co, Cu, Zn)PO_4 pigments.

No.	System	Color, Visual	Intensity, Relative
4.1	$KCo_{0,10}Zn_{0,90}PO_4$	luminous gentian blue	100
4.2	$KCo_{0,10}Cu_{0,20}Zn_{0,70}PO_4$	luminous blue	220
4.3	$KCo_{0,10}Cu_{0,45}Zn_{0,45}PO_4$	luminous gentian blue	240
4.4	$KCo_{0,10}Cu_{0,60}Zn_{0,30}PO_4$	luminous gentian blue	260
4.5	$KCo_{0,20}Zn_{0,80}PO_4$	luminous gentian blue	208
4.6	$KCo_{0,25}Zn_{0,75}PO_4$	luminous full blue	262
4.7	$KCo_{0,25}Cu_{0,38}Zn_{0,37}PO_4$	luminous full blue	367
4.8	$KCo_{0,25}Cu_{0,50}Zn_{0,25}PO_4$	luminous blue	404
4.9	$KCo_{0,30}Zn_{0,70}PO_4$	full luminous blue	314

Claims

1. $M(I)M(II)PO_4$ green, turquoise and blue pigments, where M(I) = K and/or Na and/or Li and M(II) = xZn and/or yCu and/or zCo, while $0.00 \leq x \leq 0.99$ and $0.00 \leq y \leq 0.99$ and $0.00 \leq z \leq 0.99$, where $x + z + z = 1.00$.

2. Process for preparation of the pigments mentioned in Claim 1, characterized in that mixtures of the quantities required according to the formulas in terms of alkali metal oxides, hydroxides, alkali metal phosphates or compounds yielding these upon calcining, or single or mixed alkali metal, zinc, copper or cobalt phosphates containing water of crystallization, or anhydrous, obtained by precipitation, in gases containing O_2, preferably air, are heated to temperatures of 80-1100°C, preferably 300-900°C, with or without addition of small amounts of the mineralizers promoting crystallization, the heating and/or calcining being optionally performed several times and after simultaneous grinding of the intermediate products, at uniform or rising temperature.

3. Use of the phosphate green, turquoise and blue pigments prepared according to Claim 2 for coloring of inorganic and/or organic dispersion media.